MACROSCOPIC SPACE CHARGE IN ELECTROLYTES DURING ELECTROLYSIS

C. A. REED and W. SCHRIEVER
University of Oklahoma, Norman

ABSTRACT

Since the publication of Hittorf's famous paper in 1853, it has been assumed, in general, that in every small element of volume of an electrolyte undergoing electrolysis, the sum of the charges on the negative ions is equal to the sum of the charges on the positive ions, namely, that during electrolysis macroscopic space charge does not exist. Apparently, Hittorf based this assumption on some experimental results which were obtained by Faraday in 1831.

Macroscopic space charge is known to exist in a uniformly ionized column of a gas which is conducting an electric current. Since the column of electrolyte is also uniformly ionized throughout, and since the current in each consists of positive ions moving toward the cathode together with negative ions moving toward the anode, it seems reasonable to expect that macroscopic space charges might exist in an electrolyte during electrolysis.

An apparatus which had been developed for graduate thesis research at the University of Oklahoma was perfected. Procedures were developed which permitted the accurate determination of the potential distribution along a uniform column of electrolyte during electrolysis. The potential was found to be a non-linear function of the distance from the cathode, and it was shown that this non-linearity could not be due to concentration changes brought about by the electrolysis. It was also shown that this non-linear relation could exist only if macroscopic space charges existed in the electrolyte.

The distribution of the macroscopic space charge along the column was calculated from the potential distribution. In every case it was apparent that the column of electrolyte contained four space-charge regions. Very near the cathode the charge was positive. The next quarter of the column contained negative space charge. Very near the anode the space charge was negative. The remainder of the column (about ¾ of it) contained positive space charge. The largest space charge was observed within one mm. from an anode; it required an excess of 2,000,000 Cu^{++} ions over the SO_4^{--} ions per cubic cm., an excess of only 3 ions for every 10^{12} Cu^{++} ions originally present. The space charges in other parts of the column were very much smaller than this.

The distribution of the electric field strength along the column of electrolyte was also calculated from the potential distribution. Although the magnitudes of the space charges were very small, they had very appreciable effects on the field strengths. Since this is true any direct current method for determining electrolytic conductivities must take space charge effects into account. A method for doing this was suggested.

The eight electrolytes studied were 0.0024 normal solutions of cupric sulphate, cupric chloride, zinc sulphate, zinc chloride, zinc acetate, nickel sulphate, nickel chloride, and aluminum sulphate. In each case the electrodes were made of pure metal, the metal being that of the positive ions. In each case the column of electrolyte was 40 cm. long by 8 cm. wide by 8 cm. deep.

The results of this research force one to the conclusion that macroscopic space charges do exist in an electrolyte during electrolysis, and that this phenomenon is more complicated than it is in uniformly ionized gases. It is expected that this newly discovered phenomenon will cause a reexamination of the theories concerning electrolysis.